The original article appeared in *Dalton Transactions*, 2019, 48, 2000-2012

Available at https://doi.org/10.1039/C8DT04947E

ARTICLE

Isoselenocarbonyl Complexes

Ian A. Cade,[a] Anthony F. Hill[a,*] and Caitlin M. A. McQueen[a]

Received 00th January 20xx,
Accepted 00th January 20xx

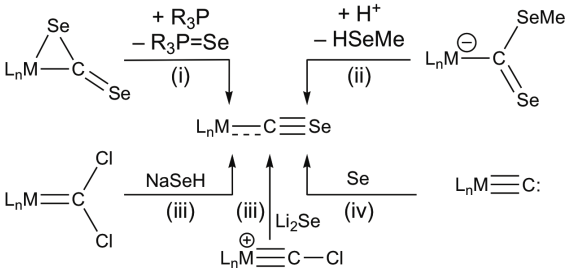
DOI: 10.1039/x0xx00000x

www.rsc.org/

The salt elimination reactions of $[NEt_4][Mo(CSe)(CO)_2(Tp^*)]$ ($[NEt_4][\mathbf{2}]$, Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) with a range of metal halide complexes ($ClML_n$) have been investigated as a possible route to isoselenocarbonyl complexes $[Mo(CSeML_n)(CO)_2(Tp^*)]$. Thus the reactions of $[NEt_4][\mathbf{2}]$ with $[RuCl(L)_2(\eta\text{-}C_5R_5)]$ provide molybdenum-ruthenium derivatives $[Mo\{CSeRu(L)_2(\eta\text{-}C_5R_5)\}(CO)_2(Tp^*)]$ (L = PPh_3, R = H **4**, L = CO, R = Me **5**), both of which were structurally characterised. The molybdenum-iron derivative $[Mo\{CSeFe(CO)_2(\eta\text{-}C_5H_5)\}(CO)_2(Tp^*)]$ (**6**) was obtained from $[NEt_4][\mathbf{2}]$ and $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$ however its formulation currently rests on spectroscopic and microanalytical data. The reaction of $[NEt_4][\mathbf{2}]$ with $[RuH(NCMe)(CO)_2(PPh_3)_2]PF_6$ affords the structurally characterised hydrido-isoselenocarbonyl complex $[Mo\{CSeRuH(CO)_2(PPh_3)_2\}(CO)_2(Tp^*)]$ (**7**) with no indication of coupling of the hydride and selenocarbonyl ligand.

Introduction

Selenocarbonyl (carbon monoselenide, CSe) complexes are exceedingly rare,[1] with current non-general synthetic routes being limited to (i) phosphine-mediated abstraction of selenium from coordinated carbon diselenide,[2] (ii) electrophilic cleavage of chalcoselenoalkoxycarbonyl ligands,[3] (iii) nucleophilic attack by hydroselenide upon dichlorocarbene[4] or chlorocarbyne[5] ligands or (iv) the addition of selenium to terminal carbido ligands[6] (Scheme 1).



Scheme 1. Synthetic routes to selenocarbonyl complexes.[1-6]

By way of contrast, until recently[7] bi- or polynuclear selenocarbonyl complexes were unknown despite binuclear thiocarbonyl complexes with bridging, semi-bridging, σ-π (4-electron) bridging and isothiocarbonyl linkages all having been previously described (Chart 1).[8]

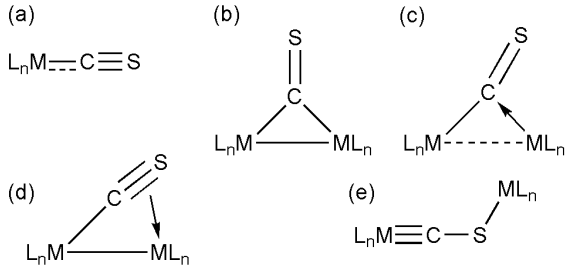


Chart 1. Thiocarbonyl coordination modes. (a) Terminal; (b) Bridging; (c) Semi-bridging; (d) σ-π-bridging; (e) Isothiocarbonyl.[8]

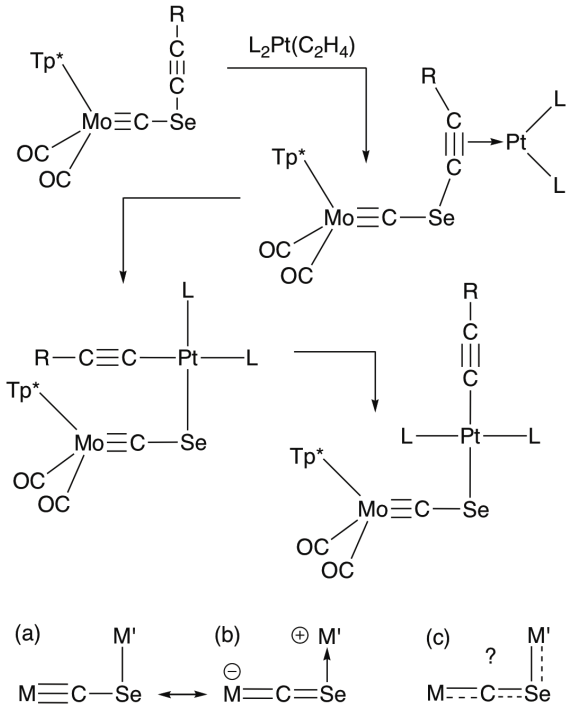
During studies of the reactivity of the alkynylselenolatocarbyne complexes $[Mo(\equiv CSeC\equiv CR)(CO)_2(Tp^*)]$ (R = C_6H_5, CMe_3, $SiMe_3$, Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate), we unexpectedly encountered the first examples of binuclear selenocarbonyl complexes in which molybdenum and platinum were bridged by an 'isoselenocarbonyl' linkage (*cf.* Chart 1e) which results from the facile cleavage of an alkynylselenoether C–Se linkage (Scheme 2).[9a,b] Furthermore, a bimetallic isoselenocarbonyl is implicated in the formation of the selenoacyl complex $[MoRh(\mu\text{-}SeCC\equiv CSiMe_3)Cl(PPh_3)(CO)_2(Tp^*)]$ *via* the reaction of $[Mo(\equiv CSeC\equiv CSiMe_3)(CO)_2(Tp^*)]$ with Wilkinson's catalyst $[RhCl(PPh_3)_3]$.[9c]

In search of a more strategic and potentially general approach to the synthesis of binuclear selenocarbonyl complexes we have considered the possibility of salt elimination

[a] *Research School of Chemistry, The Australian National University, Canberra, ACT 2601, Australia, Email: a.hill@anu.edu.au.*

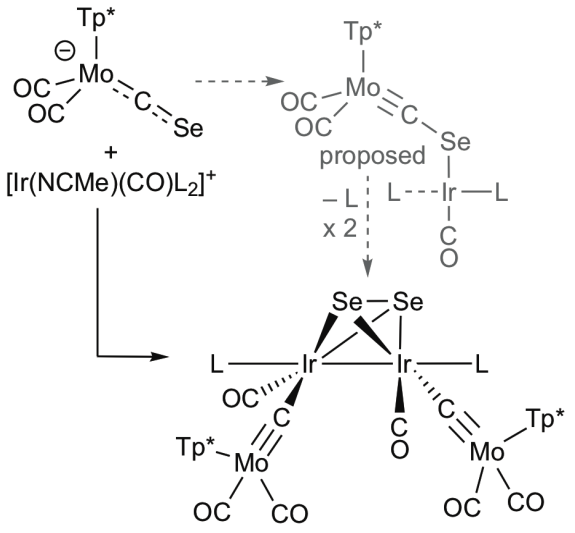
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [Crystallographic information files for CCDC 758126, 758110 – 758112]. See DOI: 10.1039/x0xx00000x

reactions of anionic selenocarbonyl complexes with metal halide complexes. Our initial exploration in this



Scheme 2. Formation of an isoselenocarbonyl linkage *via* alkynylselenolatoalkylidyne cleavage (L = PPh_3, R = ^{t}Bu, Tp* = κ^3-hydrotris(3,5-dimethylpyrazol-1-yl)borate.[9]

respect failed, though in an intriguing manner that nevertheless supported the basic strategy.[10] Whilst the reaction of Vaska's complex $[IrCl(CO)(PPh_3)_2]$ with LiSeC≡CC_6H_4Me-4 provides the simple alkynylselenolato-*Se* derivative $[Ir(SeC{\equiv}CC_6H_4Me\text{-}4)(CO)(PPh_3)_2]$,[11] the reaction of $[NEt_4][Mo(CSe)(CO)_2(Tp^*)]$[5,6b] with $[Ir(NCMe)(CO)(PPh_3)_2]BF_4$ afforded the unusual tetrametallic bis(carbido) species $(\mu_{\perp}\text{-}Se_2)[Ir_2\{C{\equiv}Mo(CO)_2(Tp^*)\}_2(CO)_2(PPh_3)_2]$ (Scheme 3) based on an Ir_2Se_2 tetrahedrane core, which can be viewed as evolving from the intended isoselenocarbonyl complex $[Ir\{SeC{\equiv}Mo(CO)_2(Tp^*)\}(CO)(PPh_3)_n]$ (n = 1,2).[10]

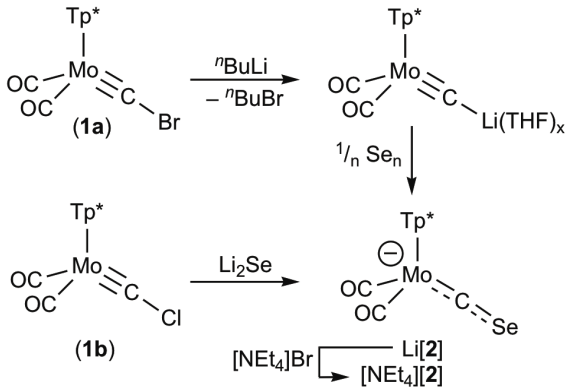


Scheme 3. C–Se Cleavage of a putative isoselenocarbonyl bridge.[10]

In contrast, reaction of $[NEt_4][Mo(CSe)(CO)_2(Tp^*)]$ with $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}COD)_2]$ results in the formation of $[Rh_2\{\mu\text{-}SeCMo(CO)_2(Tp^*)\}_2(\eta^4\text{-}COD)_2]$ in which the selenocarbonyl ligand adopts a symmetrical μ_2-Se bridging mode not yet found in thiocarbonyl chemistry.[7a] These results notwithstanding, we now report herein the successful application of the salt elimination strategy to the synthesis of a range of heterobimetallic isoselenocarbonyl complexes.

Results and Discussion

The successive treatment of Lalor's bromocarbyne complex $[Mo(\equiv CBr)(CO)_2(Tp^*)]$ (**1a**)[5] with ^{n}BuLi and grey selenium results in the formation of the salt Li[Mo(CSe)$(CO)_2(Tp^*)$] Li[**2**] (Scheme 4).[6b]



Scheme 4. Selenocarbonylate Syntheses.

Previously, the corresponding salt $[NEt_4]$[**2**] was reported to arise from the reaction of the chlorocarbyne complex $[Mo(\equiv CCl)(CO)_2(Tp^*)]$ (**1b**) with Li_2Se followed by cation metathesis,[5b] though characterisation was limited to infrared data (KBr: 1913, 1824 ν_{CO}, 1005 ν_{CSe}) and a full report has yet to emerge. Given that this salt is central to the work to be described herein, we have now completed the characterisation of $[NEt_4]$[**2**] including a crystallographic study, the results of which are summarised in Figure 1. The crystallographic characterisation of complexes with more than one type of linear diatomic ligand are often plagued by positional disorder. Thus the Cambridge Crystallographic Data Centre is rife with imprecise metrical parameters for carbonyl, nitrosyl and thiocarbonyl ligands. Previous crystallographic studies of selenocarbonyl complexes are somewhat limited, with data for the few known examples[2-4,6] being collated in Table 1 in addition to germane data from selected reference compounds involving C–Se multiple bonding. There are indications in some of these studies of the occurrence of disorder either between CO and CSe sites, or the commonly encountered transverse disorder of linear *trans*-Cl–M–CO(Se) spines. Thus the complexes $[MCl_2(CO)(CSe)(PPh_3)_2]$ (M = Ru[3a], Os[4b]) each have anomalously short C–Se bond lengths (shorter even than in free CSe[16]), consistent with some disorder between CSe and *trans* disposed

Cl ligands, which also results in an artificially lengthened M–C bond. Fortunately, the refinement of the

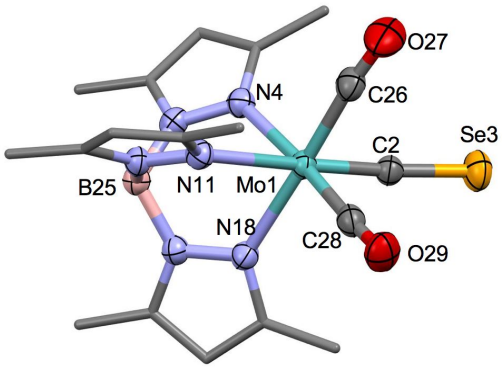


Figure 1. Molecular structure of the anion $[Mo(CSe)(CO)_2(Tp^*)]^-$ [**2**]$^-$ in a crystal of the salt [NEt_4][**2**] (60% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg.): Mo1–C2 1.857(2), Mo1–C26 1.960(3), Mo1–C28 1.967(3), Mo1–N4 2.258(2), Mo1–N11 2.263(2), Mo1–N18 2.311(2), C2–Se3 1.786(2).

Table 1. Selected structural data (Å) for selenocarbonyl complexes and related benchmark compounds.[2-4,6,12-17]

Complex[a]		M–CSe	MC–Se
$[RuCl_2(CO)(CSe)(PPh_3)_2]$[3a,d]		1.828	1.668
$[OsCl_2(CO)(CSe)(PPh_3)_2]$[4b]		1.913	1.608
$[Cr(CO)_2(CSe)(\eta^6\text{-}PhCO_2Me)]$[2g]		1.786	1.727
$[Cr(CO)_2(CSe)\{P(OMe)_3\}_3]$[2f]		1.784	1.751
$[RuCl_2(CSe)(H_2IMes)(PCy_3)]$[6c]		1.729	1.723
$[RuCl_2(CSe)(H_2IMes)(DMAP)_2]$[6c]		1.766	1.720
[NEt_4][**2**]	(Experimental)	1.857	1.786
[**2**]$^-$	(DFT-B3LYP-LANL2DZ)	1.880	1.777
Se=C=Se[12]			1.692
S=C=Se[13]			1.695
O=C=Se[14]			1.711
$(H_2N)_2C$=Se[15]			1.86
F_2C=Se[16]			1.743
C≡Se[17]			1.676

[a]H_2IMes = dihydro-*N,N'*-dimesitylimidazolylidene, DMAP = 4-dimethylaminopyridine.

structural model for [NEt_4][**2**] proceeded without any indication of positional disorder.

With the exception of 5-coordinate $[RuCl_2(CSe)(H_2IMes)(PCy_3)]$,[6c] each of the metal centres in Table 1 has a d^6-*pseudo*-octahedral configuration, however the formally zero-valent metal centre of [**2**]$^-$ is clearly the most π-basic, given the low value for ν_{CSe} (KBr: 1009 cm^{-1}). On the basis of the simple synergic model of diatomic binding, it might therefore be expected that the C–Se bond length of [**2**]$^-$ would be the longest, reflecting the most effective retrodonation into π*(CSe) orbitals. In practice the C–Se bond length for [**2**]$^-$ is indeed the longest in the series. The Mo1–C1 bond length of 1.857(2) Å is significantly (*ca* 35 e.s.d.) shorter than those to the carbonyl ligands (1.960(3), 1.967(3) Å, reflecting stronger binding to the metal centre.

Though retrodonation is expected to predominate, the increased σ-donation may account for the observed *trans* influence, such that the pyrazolyl group *trans* to the CSe ligand (Mo1–N18 2.311(2) Å) is displaced (*ca* 25 e.s.d.) from the metal centre relative to those *trans* to carbonyl ligands (Mo1–N4 2.258(2), Mo1–N11 2.263(2) Å) a feature that is reminiscent of numerous crystal structure determinations of carbyne complexes of the form $[M(\equiv CR)(CO)_2(Tp^{(*)})]$ (M = Cr, Mo, W).[18] Given that the geometry of pyrazolyl groups may be prone to solid state packing effects, it is reassuring that this *trans* influence is also computationally reproduced (DFT:B3LYP-LANL2DZ) with the Mo–N_{trans} bond length (2.399 Å) being significantly longer than the two Mo-N_{cis} bond lengths (2.325, 2.322 Å). A similar *trans* influence has been noted for the halide ligands in the complexes $[MCl_2(CO)(CSe)(PPh_3)_2]$ (M = Ru,[3a] Os[4b]) and, caveats of disorder aside, this is chemically manifest in the facile and regioselective abstraction of the chloride *trans* to the CSe ligand by silver salts of non-coordinating anions.

Table 2. Selected IR data (cm^{-1}) for the complexes $L(CO)_2M(CA)^-$ and $L(CO)_2M(CAR)$

			CA$^-$			CAR	
M	**A**	**L**		**νCO**	**R**		**νCO**
W	O	Tp*	1881	1744[SS]	Me	1958	1862[T]
Mo	O	Tp*	1891	1751[SS]	Ph	1862	1889[A]
Mo	S	Tp*	1886	1794	Me	1987	1904[SS]
Mo	S	Tp*			Ph	1899	1905
W	S	Tp	1884	1787[SS]	Me	1987	1904[NG]
Mo	Se	Tp*	1913	1824[T]	Me	1987	1905[T]
Mo	Se	Tp*			Ph	1988	1914[Cy]
Mo	Te	Tp*	1919	1835[T]	Me	1986	1902[Cy]
W	PPh	Tp*	1889	1771[T]	H	1980	1892[T]
W	PPh	Tp*			Ph	1981	1893[T]

[SS]Solid state; [T]THF; [A]acetonitrile; [NG]medium not given; [Cy]cylohexane.

The bonding of the diatomics CA (A = O, S and Se) and their coordination complexes has been interrogated at a variety of levels of sophistication.[19] In molecular orbital terms, from a coordination chemistry point of view, the orbitals of interest are the axially symmetric σ-donor 'lone pair' (σ^b) protruding from carbon and the degenerate set of π* orbitals. The σ^b-donor orbital represents the HOMO for CO and CS, with the degenerate π^b pair of orbitals below this,[19g] however for CSe and CTe the π^b orbitals become raised above the σ^b orbital. This pair of π^b orbitals is typically not discussed in a coordination chemistry context, especially for d^6-octahedral metal centres where any interaction with occupied $(t_{2g})^6$ orbitals would be unfavourable. However, given that we will subsequently consider reactions involving electrophilic attack at [**2**]$^-$, these may well play a role (*vide infra*). On proceeding from CO to CTe, the energy of the degenerate π* orbitals decreases and as with σ^b, there is a progressive reduction in the carbon character. In energetic terms CSe is therefore a superior π-acid to CO and when retrodonation occurs, electron drift from the metal to the terminal chalcogen may be expected to increase significantly. Taken together, the two key components of the classical synergic description of CO bonding are significantly enhanced for CSe and shorter M–C bonds are to be expected, attended by

significant lengthening of the C–Se bond relative to that observed in the transient free molecule.[17] A further indication of the significance of the reduction in the HOMO-LUMO gap is the paramagnetic contribution[20] to the ^{13}C NMR chemical shift of the chalcocarbonyl carbon nuclei, increasing down group 16.[21] Selenocarbonyl complexes typically give rise to downfield chemical shifts in the range δ_C = 270-360 ppm though comparatively few data have been reported to date.[1] In the case of [NEt_4][**2**] we observe a resonance at 328.9 ppm (d_6-MeCN), well downfield of that observed for the two carbonyl ligands (δ_C = 230.4). The only other known molybdenum selenocarbonyl complex is the salt K[Mo(CSe)(N^tBuAr)$_3$] (δ_C = 271.9; Ar = $C_6H_3Me_2$-3,5) reported by Cummins,[6a] which is one of a complete series of chalcocarbonyl complexes K[Mo(CE)((N^tBuAr)$_3$] (E = O, S, Se, Te) and it is noteworthy that in this higher oxidation state regime (d^4-Mo^{II}), the expected trend of increasing δ_C down group 16 is reversed. Presumably for a coordinatively unsaturated metal ligated by potent π-donor amido ligands, a significant, perhaps dominant, paramagnetic contribution also emerges from closely spaced metal orbitals that is less relevant to d^6-octahedral centres ligated by strong π-acids. The increased Se character of the σ^b orbital, the increase in energy of the π^b orbitals and the significantly enhanced π-acidity of the LUMO pair of CSe π* orbitals underpin the strategy pursued herein for the formation of bimetallic isoselenocarbonyls and follows Angelici's pioneering studies of thiocarbonyl and thiolatocarbyne chemistry.[8a,8c,22] Thus a substantial transfer of electron density from the anionic d^6-molybdenum to the selenium atom renders it especially prone to electrophilic attack. This is apparent from Figure 2 which depicts the near degenerate HOMO and HOMO-1 which clearly comprise significant selenium character (HOMO-2 is $Mo(CO)_2$ retrodative in nature). These orbitals both have Mo-C π-bonding and C-Se π-antibonding character, such that the calculated Mo-C and C-Se bond orders are 1.73 and 2.01, respectively. These observations suggest that both resonance forms shown in Figure 2 are useful in describing the MoCSe linkage, pointing towards the possibility of electrophilic attack at either the metal or (more likely) the more sterically accessible selenium.

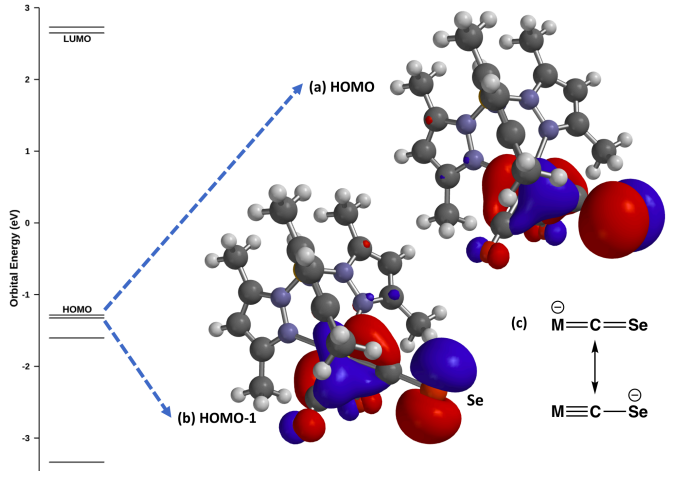
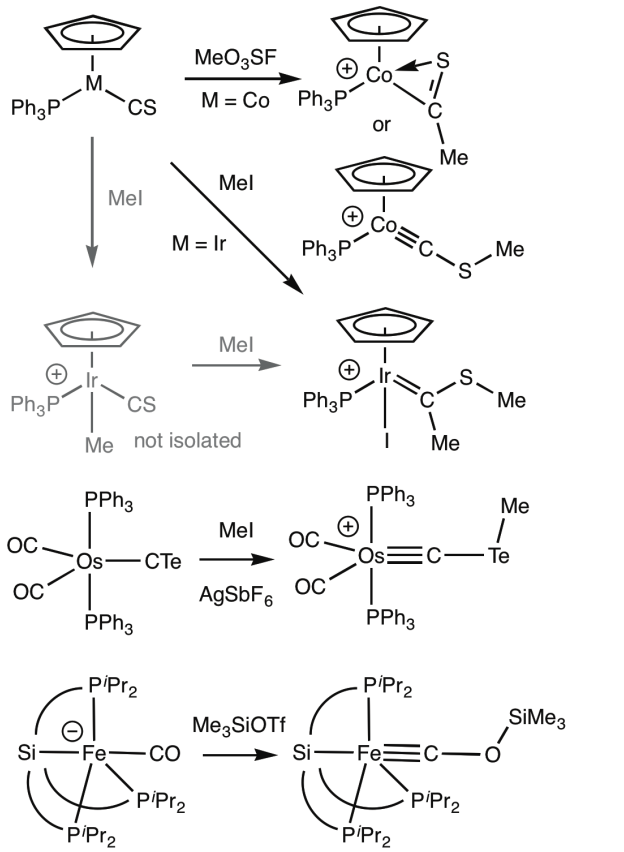


Figure 2. Selenium localised frontier orbitals of interest for [**2**]$^-$ (B3LYP-LANL2DZ). (a) HOMO; (b) HOMO-1. (c) Resonance forms to describe coordinated CSe.

In practice, the salts Li[**2**] and [NEt_4][**2**] behave somewhat differently, offering both strengths and weaknesses as synthetic intermediates. The crystalline salt [NEt_4][**2**] tends to react rather slowly due to its very limited solubility in non-halogenated solvents. The convenient *in situ* generation of more soluble Li[**2**] (Scheme 4) has the attendant problem that one equivalent of ^{n}BuBr is produced in the lithium-halogen exchange process. If the reaction is not worked up quickly, the product that eventually develops corresponds to the *n*-butylselenolatocarbyne [Mo(≡CSe^{n}Bu)$(CO)_2$(Tp*)] (**3a**) formed when [**2**]$^-$ attacks ^{n}BuBr. Treating solutions of Li[**2**] prepared *in situ*, with iodomethane readily affords the methylselenolatocarbyne complex [Mo(≡CSeMe)$(CO)_2$(Tp*)] (**3d**) which we have briefly described previously.[6b] In a similar manner, the corresponding methyltellurolato carbyne complex [Mo(≡CTeMe)$(CO)_2$(Tp*)] (**3e**) could be obtained by successive treatment of Li[**2**] with elemental tellurium and iodomethane.[23] The thiolatocarbyne analogue [Mo(≡CSMe)$(CO)_2$(Tp*)] (**3b**) has been previously reported to arise from the reaction of **1b** with methanethiol under phase transfer conditions,[5] whilst Angelici has extensively explored the synthetic versatility of the complex [W(≡CSMe)$(CO)_2$(Tp)] (**3g**; Tp = hydrotris(pyrazol-1-yl)borate) which is obtained *via* alkylation of K[W(CS)$(CO)_2$(Tp)].[22] The final member of this otherwise complete series of alkylchalcogenolato carbyne complexes [Mo(≡COMe)$(CO)_2$(Tp*)] ('**3b**') remains unknown, however Templeton has described the corresponding tungsten complex [W(≡COMe)$(CO)_2$(Tp*)] (**3f**) which arises from the reaction of [W(≡CPPh_3)$(CO)_2$(Tp*)]PF_6 with NaOMe.[24] Given that there are a number of cases where both tungsten and molybdenum analogues of various carbyne complexes [M(≡CR)$(CO)_2$(Tp*)] (M = Mo, W) have been isolated,[18a] we may include **3e** in a comparison of data for **3c**-**3f** taking into account metal-based variations in such parameters. For comparative purposes, Table 2 collates selected infrared and NMR data, respectively, for **3c**-**3f** and related complexes, to provide a means of benchmarking the effect of appending organic *cf.* metal termini to chalcocarbonyl units.

Chalcogen substituted carbynes are prevalent within group 6, primarily from the work of Angelici[23] but are otherwise rare. The alkylation of electron-rich chalcocarbonyls for later transition metals is disfavoured due to the higher d-occupancies and lower coordination numbers that make the metal centre an alternative site for electrophilic attack, *e.g.*, [IrR(CS)$(PPh_3)_2$] (R = Cl, C_6F_5) reacts with carbon electrophiles *via* oxidative addition at the iridium centre.[25] The alkylation of [Co(CS)$(PPh_3)(\eta$-$C_5H_5)$] with methyl fluorosulfonate and Na[BPh_4] has been claimed to provide the carbyne salt [Co(≡CSMe)$(PPh_3)(\eta$-$C_5H_5)$][BPh_4] however the limited characterisational data (IR, ^1H NMR)[26a] are not sufficiently definitive to exclude the alternative thioacyl formulation[26b,c] [Co(η^2-SCMe)$(PR_3)(\eta$-$C_5H_5)$][BPh_4] (Scheme 5). Outside group 6, a single structurally characterised telluromethylcarbyne is provided by the complex [Os(≡CTeMe)$(CO)_2(PPh_3)_2$]SbF_6 which does, however, result from the reaction of [Os(CTe)$(CO)_2(PPh_3)_2$] with MeI and

$AgSbF_6$.[27] Recently, remarkable siloxycarbyne complexes of iron have been reported by Peters, arising from the *O*-silylation of coordinated CO,[28] in reactions more typically encountered for early transition metals.[29]

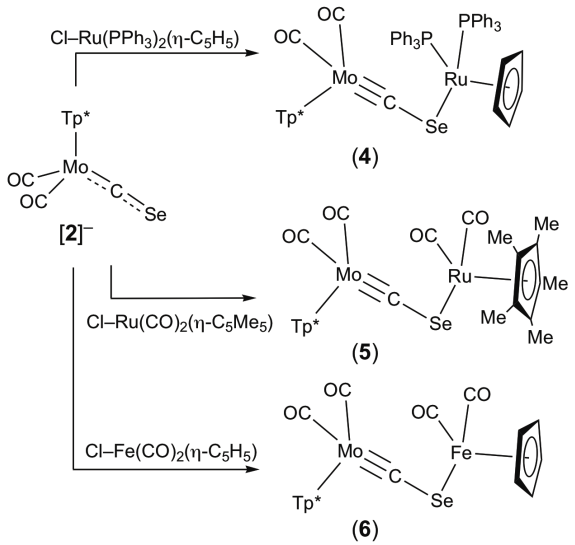


Scheme 5. Electrophilic attack at late transition metal chalcocarbonyls (presumed intermediate in grey).[24-26]

Taking together the available structural data for mononuclear chalcogenolatocarbynes '$L_nM{\equiv}CAR$' (A = O, S, Se, Te),[30] it may be concluded that (i) chalcogenolates, being positively mesomeric, (***M***$^+$) in part compromise the M-C bond order, though not as dramatically as do amino groups (2-azavinylidenes[31]); (ii) π-donation from the chalcogen to the carbyne carbon results in an increased C-A bond order and shorter C–A bond lengths than simple A–C(sp^2) or A–C(sp^3) bond lengths; (iii) there is a decrease in C–A–R angle on descending group 16, consistent with the general principle that tetrahedral sp^3 hybridisation is a concept of decreasing utility upon descending a main group (*cf.* 'p^3' hybridisation).

In general, we have found that the reactions of Li[**2**] with electrophiles proceed with poor selectivity, *e.g.*, in the reaction with Ph_3SnCl, at least eight compounds were noted by thin layer chromatography of the crude reaction mixture. Although the complex $[Mo(SnPh_3)(CO)_3(Tp^*)]$ has yet to be described, the well-known and closely related analogues $[Mo(SnPh_3)(CO)_3(L)]$ (L = $HB(pz)_3$, $MeGa(pz)_3$, $HB(mt)_3$, C_5H_5, C_5Me_5; mt = methimazolyl)[32] are each readily prepared from the reactions of the corresponding carbonylmetallate with $ClSnPh_3$. Accordingly, for the rest of this study, the salt $[NEt_4]$[**2**] was the reagent of choice, with the caveats that it is slowly attacked by dichloromethane but has poor solubility in the more innocuous solvent tetrahydrofuran and is accordingly slow to react with the electrophile of choice. Thus reactions with various metal electrophiles were typically slow at room temperature, requiring hours to days for reasonable conversions.

Our first attempt at the synthesis of an isoselenocarbonyl complex did not proceed as expected and has been discussed above and elsewhere (Scheme 3).[9] However, alternative metal electrophiles met with more success. A slow reaction ensured between $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$[33] and $[NEt_4]$[**2**] in tetrahydrofuran at 50°C to afford low yields (*ca* 20%) of a yellow compound formulated as the bimetallic complex $[Mo\{CSeRu(PPh_3)_2(\eta\text{-}C_5H_5)\}(CO)_2(Tp^*)]$ (**4**, Scheme 6) on the basis of spectroscopic data and a crystallographic study (Figure 3).



Scheme 6. Synthesis of half-sandwich molybdenum-ruthenium and molybdenum-iron isoselenocarbonyl complexes.

The infrared spectrum of **4** features two ν_{CO} bands moved to higher frequency of those for [**2**]$^-$ and devoid of any absorptions attributable to a terminal selenocarbonyl ligand. Poor solubility

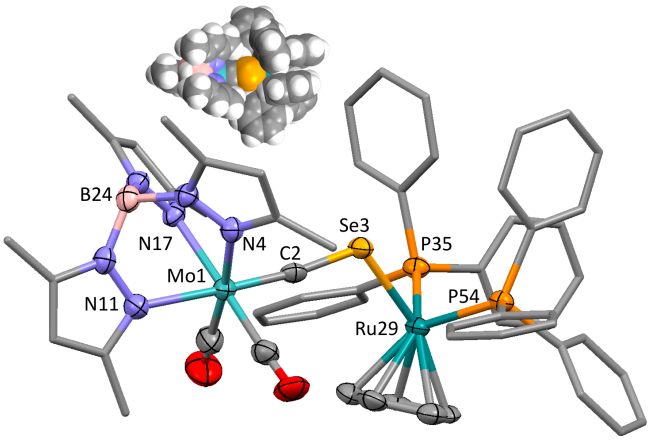
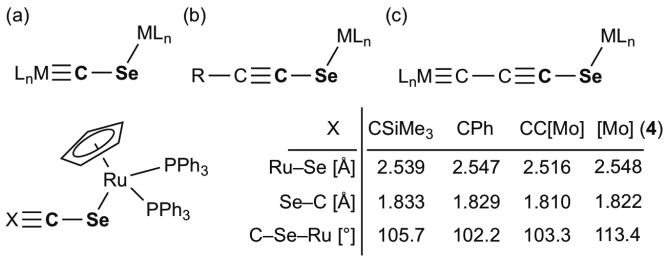


Figure 3. Molecular structure of $[Mo\{CSeRu(PPh_3)_2(\eta\text{-}C_5H_5)\}(CO)_2(Tp^*)]$ (**4**) in a crystal of **4**.$2CH_2Cl_2$ (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl and phenyl groups simplified). Selected bond lengths (Å) and angles

(deg.): Mo1–C2 1.829(6), Mo1–N4 2.240(5), Mo1–N11 2.331(5), Mo1–N17 2.262(5), C2–Se3 1.822(6), Se3–Ru29 2.5484(7), Ru29–P35 2.3325(16), Ru29–P54 2.3303(16), Mo1–C2–Se3 173.0(3), C2–Se3–Ru29 113.43(17), P35–Ru29–P54 103.86(6), Se3–Ru29–P35 86.29(4), Se3–Ru29–P54 91.64(4). Inset = space filling representation, normal to the C2–Se vector.

precluded the observation of the isoselenocarbonyl resonance of interest in the $^{13}C\{^1H\}$ NMR spectrum.

The '$Mo(CO)_2\{HB(pzMe_2)_3\}$' and '$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$' termini present their usual and generally unremarkable spectroscopic signatures.[34] Whilst structural data are not available for simple alkylselenolates of the form $[Ru(SeR)(PPh_3)_2(\eta\text{-}C_5H_5)]$, they are for the *alkynyl*selenolates $[Ru(SeC{\equiv}CR)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (R = $SiMe_3$, Ph)[35] and the *alkylidynyl*selenolate $[Ru\{SeC{\equiv}CC{\equiv}Mo(CO)_2(Tp^*)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$.[36] One might entertain an analogy with alkynylselenolate ligands (Chart 2)[11,35-37] that makes these examples particularly relevant.



X	$CSiMe_3$	CPh	CC[Mo]	[Mo] (**4**)
Ru–Se [Å]	2.539	2.547	2.516	2.548
Se–C [Å]	1.833	1.829	1.810	1.822
C–Se–Ru [°]	105.7	102.2	103.3	113.4

Chart 2. The analogy between (a) isoselenocarbonyls, (b) alkynylselenolates and (c) alkylidynylselenolates. [Mo] = $Mo(CO)_2(Tp^*)$.

Given the considerable steric bulk associated with the '**2**' substituent (see space-filling inset, Figure 3), the modest opening of the P35–Ru29–P54 angle (103.86(6)°) is not unexpected. The Se3–Ru29 separation (2.5484(7)Å) is remarkably close to those observed for the alkynylselenolate analogues,[35] though somewhat longer than that observed for the alkylidynylselenolate $\mu\text{-}C_3Se$ example (2.5164(5)Å).[36] Similarly, the Se3–C2 bond length of 1.822(6) Å is statistically identical (< 2 e.s.d.) to those for the simple alkynyl examples, thereby supporting the analogy.

The complex $[RuCl(CO)_2(\eta\text{-}C_5Me_5)]$[38] reacts similarly with $[NEt_4]$[**2**] to eventually afford the tetracarbonyl complex $[Mo\{CSeRu(CO)_2(\eta\text{-}C_5Me_5)\}(CO)_2\{HB(pzMe_2)_3\}]$ (**5**, Scheme 6), again in low yields (*ca* 20%). Although an isoselenocarbonyl resonance was not unambiguously identified in the $^{13}C\{^1H\}$ NMR spectrum, distinct resonances for the molybdenum (δ_C = 229.6) and ruthenium (δ_C = 200.5) bound carbonyl ligands were readily apparent. The molecular geometry of **5** in the solid state was established crystallographically and is presented in Figure 4. These results will be discussed below in conjunction with the other isoselenocarbonyl complexes. With considerably reduced steric clash between MoTp* and RuCp* units (*cf* **4**), repulsion between ligands on adjacent metals is still an issue such that one carbonyl ligand on ruthenium nestles between two of the dimethylpyrazolyl rings bound to molybdenum, though this is not preserved in solution. The geometry along the Mo–C–Se–Ru spine is otherwise comparable to that for **4** with the Ru1–Se1–C2 angle (103.54(12)°) being similar to that found for **4** while the angle at C2 is near to linear (172.9(2)°).

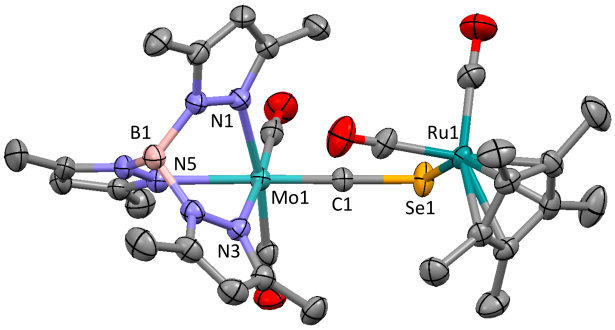
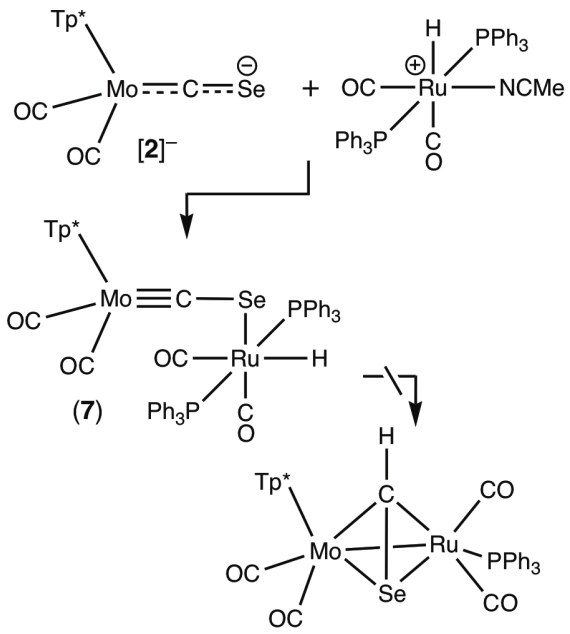


Figure 4. Molecular structure of $[Mo\{CSeRu(CO)_2(\eta\text{-}C_5Me_5)\}(CO)_2(Tp^*)]$ (**5**) in a crystal (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg.): Mo1–N1 2.239(3), Mo1–N3 2.236(3), Mo1–N5 2.300(3), Mo1–C1 1.841(4), Ru1–Se1 2.5404(4), Se1–C1 1.825(4), Ru1–Se1–C1 103.54(12).

An iron analogue of **5**, *viz* the green complex $[Mo\{CSeFe(CO)_2(\eta\text{-}C_5H_5)\}(CO)_2\{HB(pzMe_2)_3\}]$ (**6**, Scheme 6) was obtained in moderate yield (50%) from the reaction of $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$[38] with $[NEt_4]$[**2**] and although the yields were superior to those of **4** and **5**, this is off-set by the apparent light and thermal sensitivity of the complex. With time in (anaerobic) solution, the green complex becomes replaced with a predominant khaki compound that defied crystallisation attempts. Accordingly, the formulation rests on spectroscopic and microanalytical data as well as high resolution mass spectrometry, each of which are consistent with the structure proposed for **6**. Although the photo-decomposition product of **6** has not been adequately identified, it would seem most likely that decarbonylation is rapidly followed by dimerisation *via* 'selenolate' bridges, *i.e.*, $[Fe_2\{\mu\text{-}SeCMo(CO)_2\{HB(pzMe_2)_3\}_2(CO)_2(\eta\text{-}C_5H_5)_2]$. In a similar manner it has been shown that more conventional selenolates may bridge Fe–Fe bonds within the cyclopentadienyl/carbonyl class of compound, *e.g.*, $[Fe_2(\mu\text{-}SeR)_2(CO)_2(\eta\text{-}C_5H_5)_2]$.[39] Further support for this unusual μ-*Se* bridging mode is provided by the product of the reaction of $[Rh_2(\mu\text{-}Cl)_2(\eta^4\text{-}C_8H_{12})_2]$ with $[NEt_4]$[**2**] which was identified as the tetrametallic species $[Rh_2\{\mu\text{-}SeCMo(CO)_2\{HB(pzMe_2)_3\}\}_2(\eta^4\text{-}C_8H_{12})_2]$.[7a]

Thioformyl ligands remain rare, though the synthetic utility of those that have been isolated has been amply demonstrated.[40] Although a small number of selenoaroyl and selenocarbamoyl complexes have been reported,[41] selenoformyls (and indeed telluroformyls) remain unknown. The migratory coupling of selenocarbonyl and alkynyl ligands has, however, been suggested as a mechanistic possibility for the formation of an unusual selenopropionoyl complex $[MoRh(\mu\text{-}SeCCCSiMe_3)(CO)_2(PPh_3)Cl\{HB(pzMe_2)_3\}]$.[9c] We therefore turned our attention to the possible synthesis of a hydrido-isoselenocarbonyl complex in an attempt to observe whether the formation of binuclear selenoformyl complex was a viable alternative. The salt $[RuH(NCMe)(CO)_2(PPh_3)_2]PF_6$[42] reacts slowly with $[NEt_4]$[**2**] to afford the orange compound $[Mo\{CSeRuH(CO)_2(PPh_3)_2\}(CO)_2\{HB(pzMe_2)_3\}]$ (**7**, Scheme 7).



Scheme 7. Synthesis of a hydrido(μ_2-isoselenocarbonyl) complex **7**.

The appearance of a triplet resonance at δ_H = –5.42 in the ^{1}H NMR spectrum attests to the hydride ligand remaining bound to ruthenium, *cis* to two chemically equivalent and mutually *trans* phosphine ligands ($^2J_{PH}$ = 19.3 Hz). The appearance of two ruthenium associated ν_{CO} infrared absorbances (2040, 1951 cm^{-1}) indicates a *cis*-Ru(CO)$_2$ geometry, pointing towards the stereochemistry indicated in Scheme 7. This was confirmed by a crystallographic study the results of which are summarised in Figure 5. As regards the ruthenium coordination sphere, the overall topology is similar to that described by James for the more conventional selenolate complex [RuH(SePh)(CO)$_2$(PPh$_3$)$_2$] (δ_H = –4.75, $^2J_{PH}$ = 19.8 Hz) obtained *via* the oxidative addition of benzene selenol to [Ru(CO)$_2$(PPh$_3$)$_3$],[43] which is analogous to the

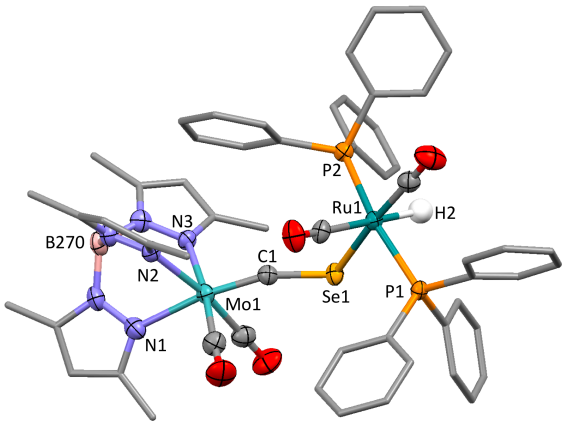


Figure 5. Molecular structure of [Mo{CSeRuH(CO)$_2$(PPh$_3$)$_2$}(CO)$_2$(Tp*)] (**7**) in a crystal (50% displacement ellipsoids, hydrogen atoms omitted, pyrazolyl and phenyl groups simplified). Selected bond lengths (Å) and angles (deg.): Mo1–N1 2.256(6), Mo1–N2 2.309(7), Mo1–N3 2.247(5), Mo1–C1 1.840(7), Ru1–Se1 2.5992(9), Ru1–H2 1.67(9), Se1–C1 1.838(7), Se1–Ru1–H2 88(3), Ru1–Se1–C1 115.2(2).

geometry that was crystallograhically confirmed for the sulfur analogue [RuH(SC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2$].[43]

Table 3 collates selected data for the Mo–C–Se–M' spines of isoselenocarbonyl complexes prepared herein in addition to data for the precursor [NEt$_4$][**2**] and the two previously reported molybdenum platinum complexes, *cis* and *trans* [Mo{CSePt(C≡C^{t}Bu)(PPh$_3$)$_2$}(CO)$_2${HB(pzMe2)$_3$}].[9] First and foremost, it must be stressed that the HB(pzMe$_2$)$_3$ scorpionate is an especially bulky ligand (cone angle ≈ 225°)[18] and its steric profile will be expected to exert an effect on the geometrical features, not only with respect to the molybdenum coordination sphere but also through steric congestion with ligands on the adjacent metal. A second feature to bear in mind is that deformation of alkylidyne ligands from linearity is quite common[18a] and is in most cases a soft response to crystal packing effects and non-bonding interactions. Thus if isoselenocarbonyl complexes are considered as a special case of carbyne complex, it would be unwise to over-interpret deviations from linearity.

The data presented in Table 3 show a loose correlation between associated Mo–C and C–Se bond lengths (Figure 6), wherein elongation of the C–Se bond is accompanied by contraction of the MoC bond as it acquires more carbyne character. The outlier in this generalisation is the complex **4** which involves the most π-basic metal centre, 'Ru(PPh$_3$)$_2$(η-C$_5$H$_5$)' however this is also the most sterically encumbered which is also reflected in the larger C–Se–Ru angle (113.4°). The tetrametallic complex [Rh$_2${μ-SeCMo(CO)$_2$(Tp*)}$_2$(η^4-COD)$_2$][7a] in which the three-coordinate selenium atoms bridge two rhodium centres has, as expected, the longest C–Se and shortest Mo≡C bond lengths.

Table 3. Selected Spectroscopic and Structural Data for Isochalcocarbony Complexes [Mo(CSeML$_n$)(CO)$_2$(Tp*)] and Isothiocarbonyl Complexes

ML$_n$	ν_{MoCO} [cm^{-1}]	δ_{MoC} [ppm]	r_{MoC} [Å]	r_{CSe} [Å]	r_{SeM} [Å]	<$_{CSeM}$ [°]
[**2**]$^-$	1908, 1818	328.9	1.857	1.786	–	–
CH$_3$	1987, 1905	269.3	1.823	1.848	1.955	–
cis-Pt(CC^{t}Bu)(PPh$_3$)$_2$[9]	1957, 1875	297.5	1.832	1.836	2.489	105.4
trans-Pt(CC^{t}Bu)(PPh$_3$)$_2$[9]	1952, 1868	302.5	1.834	1.828	2.491	104.9
Rh(η^4-C$_8$H$_{12}$)[a, 7a]	1964, 1880	–	1.815	1.854	2.528	95.5
Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) (**4**)	1939, 1854	–	1.829	1.822	2.549	113.4
Ru(CO)$_2$(η-C$_5$Me$_5$) (**5**)	1965, 1872	–	1.841	1.825	2.540	103.5
Fe(CO)$_2$(η-C$_5$H$_5$) (**6**)	1993,1879	296.8	–	–	–	–
RuH(CO)$_2$(PPh$_3$)$_2$ (**7**)	1986, 1873	308.6	1.840	1.838	2.599	115.2
ML$_n$		δ_{MC}	r_{MC}	r_{CS}	r_{SM}	<$_{CSM}$
Mo$_2$(μ-CS)(NR$_2$)$_6$[b, 8p]	–	293.5	1.751	1.757	2.289	130.5
Cr$_2$(μ-CS)(CO)$_8$(PhMe)[8b]	–	–	1.747	1.605	2.486	110.5

[a]Dimeric with μ_2-Se bridges. [b]NR$_2$ = N(C$_6$H$_3$Me$_2$-3,5)^{t}Bu

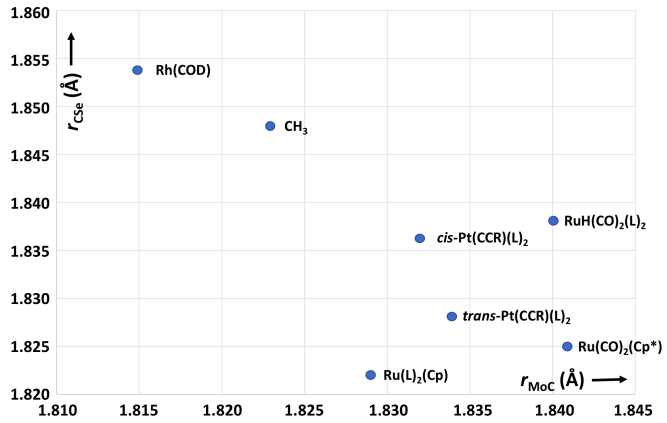


Figure 6. Relationship between r_{MoC} and r_{CSe} bond lengths for complexes of the form [Mo(CSeR)(CO)$_2$(Tp*)] (R = Me, ML$_n$) featuring CSe bridges (L = PPh$_3$, R = ^{t}Bu, COD = η^4-1,5-cyclo-octadiene).

Although very distinct from the termini employed in this study, the two complexes [Mo$_2$(μ-CS)(NR$_2$)$_6$] (NR$_2$ = N(C$_6$H$_3$Me$_2$-3,5)^{t}Bu)[8p] and [Cr$_2$(μ-CS)(CO)$_8$(PhMe)][8b] present useful comparators as extremes in the degree of CS activation. The former, being diamagnetic, calls for canonical form A (Chart 3) with the CS unit spanning formally Mo^{VI} and Mo^{IV} centres and for which, although sought, a ν_{CS} absorption was not located, consistent with extensive reduction in the C–S multiple bond character. The latter is, however, better described by canonical form B for which two d^6-Cr^0 centres are envisaged, with a ν_{CS} absorption observed at 1205 cm^{-1}, *i.e.*, within the range typical of C-S multiple bonding.

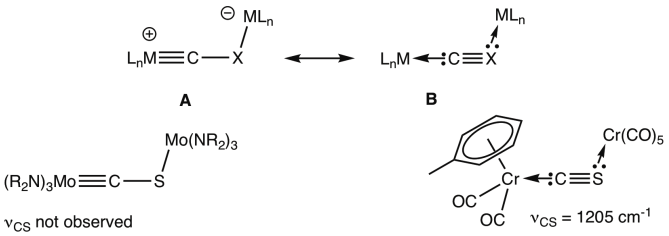


Chart 3. Canonical forms for the extremes of CA coordinative activation (X = S, Se) and exemplars.

Zhang and King have extensively investigated polymetallic thiocarbonyl complexes using DFT methods for a host of metals[44] and it is worth noting that amongst this plethora of, as yet, hypothetical molecules, those involving isothiocabonyl linkages are somewhat scarce. The exceptions appear to be half-sandwich examples [V$_2$(CS)$_2$(CO)$_x$(η-C$_5$H$_5$)$_2$] (x = 4,5),[44a] [Cr$_2$(CS)$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$][44b] and [Mn$_2$(CS)$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$].[44c] The isothiocarbonyl linkage provides a total of 4 electrons to the two metals as does the μ:σ–π side on coordination mode (Chart 1d) and in general it is this latter coordination mode that is preferred, especially (but not exclusively) when the two metals are also directly bonded. The steric bulk of the Tp* ligand disfavours direct metal-metal bond formation, whilst the less sterically imposing Tp ligand is able to support both μ:σ–π[8g] and semi bridging[8h] thiocarbonyls in the complexes [MoW(μ-CS)(CO)$_4$(η^5-C$_9$H$_7$)(Tp)] and [WAu(μ-CS)(CO)$_2$(PPh$_3$)(Tp)], respectively. We therefore anticipate that isoselenocarbonyl linkages, as reported herein, are likely to be less stable than the alternative but *kinetically* disfavoured μ:σ–π mode. It is however noteworthy that the one instance where such μ:σ–π selenocarbonyl coordination has been inferred was as an intermediate *en route* to C-Se cleavage.[10] Furthermore, the reaction of [Re(CS)(CO)$_2$(η-C$_5$H$_5$)] with [Re(THF)(CO)$_2$(η-C$_5$H$_5$)] which affords the μ-carbido complex [Re$_2$(μ-C)(CO)$_4$(η-C$_5$H$_5$)$_2$] and [Re(η^2-S$_2$)(CO)$_2$(η-C$_5$H$_5$)][45] is presumed to proceed *via* bimetallic intermediates akin to [Mn$_2$(CS)$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$], as envisaged by King.[44c] It therefore remains to be seen, which metals might allow isolation of this alternative bridging mode without C-chalcogen bond cleavage.

Conclusions

Despite previous isoselenocarbonyl complexes either arising inadvertently or alternatively evolving to other products, their strategic synthesis is indeed viable via simple salt elimination reactions between a selenocarbonylate and judiciously chosen metal halido complex. On the basis of trends in the variation of Mo–C and C–Se bond lengths, as well as ^{13}C NMR chemical shifts, the isoselenocarbonyl linkage L$_n$MoCSeML$_n$ is less 'carbyne like' than the simple alkynylselenolatocarbyne [Mo(CSeMe)(CO)$_2$(Tp*)], retaining a degree of C–Se multiple bonding character. It should be noted, however that the termini included here and previously are based on d^6-octahedral or d^8 square planar geometries for which the high d-occupancies are expected to minimise any Se(pπ)-M(dπ) π-donation component, *i.e.*, other trends may emerge if isoselenocarbonyl chemistry is explored for earlier metals with vacant t_{2g}-type orbitals.

The examples of isoselenocarbonyls reported here appear to all be indefinitely stable under mild conditions. Given that alkynylselenolate, alkynylselenolatocarbyne and (in one instance) an isoselenocarbonyl ligand have all previously been shown to undergo facile C–Se cleavage, rich ligand base chemistry may be anticipated for this class of compound.

Experimental

General Considerations. All manipulations were carried out under an atmosphere of pre-purified and dried dinitrogen using standard Schlenk and vacuum line techniques unless otherwise indicated. Dichloromethane and acetonitrile were dried over calcium hydride and distilled under dinitrogen. Paraffins and ethers were distilled from Na/benzophenone under dinitrogen. Absolute ethanol was dried over iodine-activated magnesium and distilled under dinitrogen. Reactions were carried out at room temperature unless otherwise stated. NMR spectra were recorded on Varian Inova 300 or Mercury 300 spectrometers (^{1}H, 299.9; ^{31}P{^{1}H}, 121.5; ^{13}C{^{1}H}, 75.42; ^{77}Se{^{1}H}, 57.26 MHz). ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported relative to residual solvent peaks. ^{31}P{^{1}H} and ^{77}Se{^{1}H} NMR chemical shifts are reported relative to external references (85% H$_3$PO$_4$, Ph$_2$Se$_2$). 't^v' refers to virtual triplet resonances observed for

trans-bis(triphenylphosphine) complexes with the apparent J_{PC} couplings indicated. Elemental microanalytical data were provided by the ANU Research School of Chemistry microanalytical service. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the Research School of Chemistry mass spectrometry service, with assignments confirmed by simulation of isotopic distributions. Data for X-ray crystallography were collected with a Nonius Kappa CCD diffractometer and structures solved and refined by direct methods. The following compounds were prepared according to published methods: NaSeH,[46] $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$,[33] $[RuCl(CO)_2(\eta\text{-}C_5Me_5)]$,[47] $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$,[38] and $[RuH(NCMe)(CO)_2(PPh_3)_2][PF_6]$.[42] All other reagents were used as received from commercial sources.

Synthesis of $[NEt_4][Mo(CSe)(CO)_2\{HB(pzMe_2)_3\}]$ $[NEt_4][2]$ – A suspension of $[Mo(\equiv CBr)(CO)_2\{HB(pzMe_2)_3\}]$ (**1a**: 2.00 g, 3.70 mmol) in EtOH (60 mL) was cooled with stirring to 0 °C and treated with an ethanolic solution of NaSeH[46] (7.50 mL, 0.50 M, 3.75 mmol). The mixture was raised to room temperature, stirred for 30 min, and treated with a second aliquot of NaSeH (3.75 mmol). The mixture was stirred for 16 hrs, before being transferred via a cannula filter into a degassed aqueous solution of $[NEt_4]Br$ (3.12 g, 14.8 mmol in 100 mL H_2O). The product formed instantly as a yellow floccular precipitate, which was washed successively with degassed EtOH (3 x 50 mL) and H_2O (3 x 50 mL). NB: Liberal washing is necessary to remove any residual NaSeH, which upon exposure to air is immediately converted to superficial red selenium. The resulting solid was recrystallised from acetonitrile. Yield: 2.17 g (87%). IR (KBr, cm^{-1}): 1911, 1826 ν_{CO}, 1540 ν_{CN}, 1009 ν_{CSe}. IR (MeCN, cm^{-1}): 1908, 1818 ν_{CO}, 1543 ν_{CO}. NMR (CD_3CN, 298 K) ^1H: δ_H = 2.27 (s, 3 H, $pzCH_3$), 2.30 (s, 3 H, $pzCH_3$), 2.32 (s, 6 H, $pzCH_3$), 2.66 (s, 6 H, $pzCH_3$), 5.66 (s, 1 H, pzH), 5.76 (s, 2 H, pzH). $^{13}C\{^1H\}$: δ_C = 328.9 (MoCSe), 230.4 (CO), 152.6, 151.5, 145.2, 144.6 [2:1:1:2, $C^{3,5}$(pz)], 106.1, 105.9 [1:2, C^4(pz)], 15.5, 14.8, 12.7, 12.6 ($pzCH_3$). ESI-MS (-ve ion, MeCN): *m/z* = 541.0 $[M]^-$. Accurate Mass: Found 540.0128 $[M]^-$, Calcd. for $C_{18}H_{22}{}^{11}B^{98}Mo^{14}N_6O_2{}^{80}Se$: 540.0117. Anal. Found: C, 46.26; H, 6.39; N, 14.44%. Calcd for $C_{26}H_{42}BMoN_7O_2Se$: C, 46.58; H, 6.31; N, 14.63%. *Crystal data for* $C_{26}H_{42}BMoN_7O_2Se$: M_r = 670.38, triclinic, *P*–1 (No. 2), *a* = 9.9705(2), *b* = 9.9833(2), *c* = 16.6900(3) Å, α = 94.7874(15)°, β = 94.4024(13)°, γ = 111.7729(11)°, *V* = 1526.95(5) Å^3, *Z* = 2, D_{calcd} = 1.458 Mg m^{-3}, μ(Mo Kα) = 1.656 mm^{-1}, *T* = 200(2) K, yellow block, 0.12 x 0.27 x 0.41 mm, 8,904 independent reflections. F^2 refinement, R_1 = 0.035, wR_2 = 0.078 for 6239 reflections ($I > 2\sigma(I)$), $2\theta_{max}$ = 60°), 343 parameters, CCDC 758110.

Synthesis of $[Mo(\equiv CSeMe)(CO)_2\{HB(pzMe_2)_3\}]$ (3a). – A solution of $[Mo(\equiv CBr)(CO)_2\{HB(pzMe_2)_3\}]$ (**1**: 0.200 g, 0.370 mmol) in tetrahydrofuran (10 mL) was cooled (dry ice/acetone) and treated with ^{n}BuLi (0.15 mL, 2.50 M in n-hexane, 0.38 mmol). After stirring for 15 min, elemental (grey) selenium (0.029 g, 0.37 mmol) was added and stirring continued at this temperature for a further 15 min. The resulting solution of Li[**2**] was allowed to warm to room temperature, treated with iodomethane (0.03 mL, 0.48 mmol) and stirred for a further 15 min. The solvent was removed under reduced pressure, and the residue was then extracted with DCM and chromatographed on silica gel using a 10% DCM/n-hexane mixture as eluent, to provide a pinkish-brown band. The solvent was removed under reduced pressure, and the product recrystallised from n-hexane. Yield: 0.084 g (41%). IR (*n*-hexane, cm^{-1}): 1991, 1910 ν_{CO}. IR (THF, cm^{-1}): 1986, 1902 ν_{CO}. NMR ($CDCl_3$, 298 K) ^1H: δ_H = 2.30 (s, 3 H, $pzCH_3$), 2.34 (s, 6 H, $pzCH_3$), 2.35 (s, 3 H, $SeCH_3$), 2.55 (s, 6 H, $pzCH_3$), 2.60 (s, 3 H, $pzCH_3$), 5.71 (s, 1 H, pzH), 5.83 (s, 2 H, pzH). $^{13}C\{^1H\}$: δ_C = 269.3 (Mo≡C), 226.2 (CO), 151.4, 151.1, 145.0, 144.4 [$C^{3.5}$(pz)], 106.3, 106.2 [C^4(pz)], 15.9, 14.6, 12.7, 9.7 ($pzCH_3$), 1.0 ($SeCH_3$). These data were consistent with those previous published.[6b]

Synthesis of $[Mo\{CSeRu(PPh_3)_2(\eta\text{-}C_5H_5)\}(CO)_2\{HB(pzMe_2)_3\}]$ (4) – A suspension of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$[33] (0.217 g, 0.297 mmol) and $[NEt_4][Mo(CSe)(CO)_2\{HB(pzMe_2)_3\}]$ ($[NEt_4][$**2**$]$: 0.200 g, 0.298 mmol) in THF (20 mL) was heated to 50 °C and stirred magnetically for 60 hours. The resultant brown supernatant was separated from unreacted $[NEt_4][$**2**$]$ via cannula filtration, and freed of volatiles under reduced pressure. The product was obtained by recrystallisation of the residue from a mixture of dichloromethane and ethanol (1:1, – 18 °C). Yield: 0.073 g (20%) IR (KBr, cm^{-1}): 1939, 1843 ν_{CO}, 1543 ν_{CN}. IR (THF, cm^{-1}): 1939, 1854 ν_{CO}, 1544 ν_{CN}. NMR (CD_2Cl_2, 298 K) ^1H: δ_H = 2.33 (s, 3 H, $pzCH_3$), 2.34 (s, 6 H, $pzCH_3$) 2.35 (s, 3 H, $pzCH_3$), 2.71 (s, 6 H, $pzCH_3$), 4.56 (s, 5 H, C_5H_5), 5.72 (s, 1 H, pzH), 5.80 (s, 2 H, pzH), 7.12-7.37 (m, 30 H, C_6H_5). $^{13}C\{^1H\}$: δ_C = 232.6 (CO), 152.5, 151.3, 145.4, 144.6 [2:1:1:2, $C^{3,5}$(pz)], 106.1 [C^4(pz)], 82.5 (C_5H_5), 16.2, 14.8, 12.9, 12.7 (2:1:2:1, $pzCH_3$). The Mo≡C resonance was not unambiguously identified due to a poor signal to noise ratio. $^{31}P\{^1H\}$: δ_P = 42.5. ESI-MS (+ve ion, MeCN): *m/z* = 1233.5 $[M]^+$, 690.5 $[Ru(PPh_3)_2(C_5H_5)]^+$. Accurate Mass: Found 1234.1377 $[M]^+$. Calcd. for $C_{59}H_{57}{}^{11}B^{98}MoN_6O_2P_2{}^{102}Ru^{80}Se$ 1234.1374. Anal. Found C, 52.07; H, 4.45; N, 5.78%. Calcd. for $C_{59}H_{57}BMoN_6O_2P_2RuSe.(CH_2Cl_2)_2$: C, 52.28; H, 4.39; N, 6.00%. *Crystal data for* **4**.$(CH_2Cl_2)_2$: $C_{59}H_{57}BMoN_6O_2P_2RuSe.(CH_2Cl_2)_2$: M_r = 1400.73, triclinic, *P*–1 (No. 2), *a* = 13.5618(3), *b* = 15.3628(4), *c* = 15.6564(4) Å, α = 83.7605(13)°, β = 75.6795(15)°, γ = 78.2821(15)°, *V* = 3088.86(13) Å^3, *Z* = 2, $D_{calcd.}$ = 1.506 Mg m^{-3}, μ(Mo Kα) = 1.309 mm^{-1}, *T* = 200(2) K, yellow block, 0.12 x 0.27 x 0.41 mm, 8,904 independent reflections. F^2 refinement, R_1 = 0.035, wR_2 = 0.078 for 6,239 reflections ($I > 2\sigma(I)$), $2\theta_{max}$ = 50°), 343 parameters, CCDC 758111.

Synthesis of $[Mo\{CSeRu(CO)_2(\eta\text{-}C_5Me_5)\}(CO)_2\{HB(pzMe_2)_3\}]$ (5) – A mixture of $[RuCl(CO)_2(\eta\text{-}C_5Me_5)]$ (0.031 g, 0.095 mmol) and $[NEt_4][Mo(CSe)(CO)_2\{HB(pzMe_2)_3\}]$ ($[NEt_4][$**2**$]$: 0.063 g, 0.094 mmol) was dissolved in THF (10 mL) and stirred for 12 days. The resulting red supernatant was separated from unreacted $[NEt_4][$**2**$]$ via cannula filtration, and freed of volatiles under reduced pressure. The residue was re-dissolved in THF and chromatographed on silica gel using a 10% mixture of THF in *n*-hexane as eluent, to provide a red band. The solvent was removed under reduced pressure, and the product crystallised

from a mixture of DCM and ethanol (1:2, 25°C). Yield: 0.036 g (46%). IR (KBr, cm^{-1}): 2022, 1965, 1953, 1872 ν_{CO}, 1542 ν_{CN}. IR (THF, cm^{-1}): 2026, 1975, 1961, 1879 ν_{CO}, 1543 ν_{CN}. NMR (C_6D_6, 298 K) ^{1}H: δ_H = 1.44 (s, 15 H, C_5CH_3), 2.11 (s, 3 H, $pzCH_3$), 2.16 (s, 6 H, $pzCH_3$), 2.48 (s, 3 H, $pzCH_3$), 2.99 (s, 6 H, $pzCH_3$), 5.40 (s, 1 H, pzH), 5.59 (s, 2 H, pzH). ^{13}C{^{1}H}: δ_C = 229.6 (MoCO), 200.5 (RuCO), 151.5, 151.4, 144.1, 143.6 [2:1:1:2, $C^{3,5}$(pz)], 106.3, 106.2 [1:2, C^4(pz)], 99.7 (η^5-C_5) 16.4, 14.9, 12.7, 12.5 (2:1:2:1, $pzCH_3$), 9.6 ($C_5\underline{C}H_3$). The Mo≡C resonance was not unambiguously identified due to a poor signal to noise ratio. ESI-MS (+ve ion, MeCN): *m/z* = 855.4 $[M + Na]^+$, 799.4 $[M–2CO+Na]^+$. Anal. Found: C, 42.96; H, 4.41, N, 9.87%. Calcd. for $C_{30}H_{37}BMoN_6O_4RuSe$: C, 43.26; H., 4.48; N, 10.10%. *Crystal data for* **5**: $C_{30}H_{37}BMoN_6O_4RuSe$: M_r = 832.44, monoclinic, $P2_1$, *a* = 9.5378(2), *b* = 18.6556(2), *c* = 10.5052(2) Å, β = 15.5514(8)°, *V* = 1686.41(5) Å^3, *Z* = 2, $D_{calcd.}$ = 1.639 Mg m^{-3}, μ(Mo Kα) = 1.94 mm^{-1}, *T* = 200(2)K, orange plate, 0.34 x 0.23 x 0.11 mm, 7,692 independent reflections. F^2 refinement, R_1 = 0.025, wR_2 = 0.066 for 6,643 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 398 parameters, CCDC 758112.

Synthesis of [Mo{CSeFe(CO)$_2$(η-C$_5$H$_5$)}(CO)$_2${HB(pzMe$_2$)$_3$}] (6) - The product proved to be both thermally and light sensitive. Accordingly, in the following preparation light exposure was minimised by the use of aluminium foil and subdued lighting. A mixture of $[FeCl(CO)_2(\eta\text{-}C_5H_5)]$[38] (0.064 g, 0.30 mmol) and $[NEt_4][Mo(CSe)(CO)_2\{HB(pzMe_2)_3\}]$ ($[NEt_4]$[**2**]: 0.200 g, 0.298 mmol) in THF (15 mL) was stirred for 96 hours. The dark green supernatant was separated from unreacted $[NEt_4]$[**2**] via cannula filtration and freed of volatiles under reduced pressure. The residue was redissolved in THF and chromatographed on neutral alumina using a 20% mixture of THF in *n*-hexane as eluent. A green band was collected, and the solvent removed under reduced pressure to provide a dark green microcrystalline powder. Anaerobic solutions of this complex deteriorate slowly and failed to provide crystallographic quality crystals. Yield: 0.108 g (50%). IR (Nujol, cm^{-1}): 2033, 1992, 1960, 1877 ν_{CO}, 1542 ν_{CN}. IR (*n*-hexane, cm^{-1}): 2035, 1993, 1961, 1879 ν_{CN}. NMR (C_6D_6, 298 K) ^{1}H: δ_H = 2.10 (s, 3 H, $pzCH_3$), 2.15 (s, 6 H, $pzCH_3$), 2.42 (s, 3 H, $pzCH_3$), 2.86 (s, 6 H, $pzCH_3$), 4.32 (s, 5 H, C_5H_5), 5.41 (s, 1 H, pzH), 5.57 (s, 2 H, pzH). ^{13}C{^{1}H}: δ_C = 296.8 (MoCSe), 230.3 (MoCO), 213.3 (FeCO), 151.8, 151.2, 144.5, 143.8 [2:1:1:2, $C^{3,5}$(pz)], 106.4 [C^4(pz)], 84.9 (C_5H_5), 16.2, 14.9, 12.6, 12.5 (2:1:2:1, $pzCH_3$). ESI-MS (+ve ion, MeCN) *m/z*: 756.4 $[M+K]^+$, 740.4 $[M+Na]^+$, 606.5 $[M–4CO]^+$. Accurate Mass: Found 719.9775 $[M]^+$. Calcd. For $C_{25}H_{27}{}^{11}B^{56}Fe^{98}Mo^{14}N_6O_4{}^{80}Se$: 719.9756. Anal. Found: C, 41.44; H, 4.36; N, 10.82%. Calcd. for $C_{25}H_{47}BFeMoN_6O_4Se$: C, 41.87; H, 3.80; N, 11.72%.

Synthesis of [Mo{μ-CSeRuH(CO)$_2$(PPh$_3$)$_2$}(CO)$_2$-{HB(pzMe$_2$)$_3$}] (8) – A mixture of $[RuH(NCMe)(CO)_2(PPh_3)_2][PF_6]$ (0.259 g, 0.298 mmol) and $[NEt_4][Mo(CSe)(CO)_2\{HB(pzMe_2)_3\}]$ ($[NEt_4]$[**2**]: 0.200 g, 0.298 mmol) in THF (20 mL) was stirred for 72 hours, filtered and freed of volatiles under reduced pressure. The residue was redissolved in dichloromethane and chromatographed on silica gel using a 10% mixture of dichloromethane in n-hexane as eluent to provide an orange band. The solvent was removed under reduced pressure, and the product was crystallised from a mixture of toluene and *n*-hexane (1:2, 25°C). Yield: 0.081g (22%). IR (KBr, cm^{-1}): 2040, 1988, 1951, 1865 ν_{CO}; 1544 ν_{CN}. IR (THF, cm^{-1}): 2042, 1986, 1954, 1873 ν_{CO}, 1543 ν_{CN}. NMR (C_6D_6, 298 K) ^{1}H: δ_H = –5.42 (t, 1 H, RuH, $^2J_{PH}$ = 19.3 Hz), 2.11 (s, 3 H, $pzCH_3$), 2.25 (s, 6 H, $pzCH_3$), 2.42 (s, 6 H, $pzCH_3$), 2.53 (s, 3 H, $pzCH_3$), 5.36 (s, 1 H, pzH), 5.53 (s, 2 H, pzH), 6.96-7.86 (m, 30 H, C_6H_5). ^{13}C{^{1}H}: δ_C = 308.6 (Mo≡C), 229.9 (MoCO), 199.0 (RuCO, $^2J_{PC}$ not resolved, second RuCO resonance not unambiguously identified), 152.5, 151.5, 143.7, 143.5 [2:1:1:2, $C^{3,5}$(pz)], 134.7 (t^v, $C^{2,6}$(C_6H_5), J_{PC} = 6), 134.6 (t^v, C^1(C_6H_5), J_{PC} = 24 Hz), 130.3 [C^4(C_6H_5)], 128.5 [$C^{3,5}$(C_6H_5), assignment equivocal due to overlap with C_6D_6 resonance], 106.3, 106.1 [1:2, C^4(pz)], 16.6, 14.9, 12.8, 12.5 (2:1:2:1, $pzCH_3$). ^{31}P{^{1}H}: δ_P = 40.3. ESI-MS (+ve ion, MeCN): *m/z* = 1245.6 $[M+Na]^+$. Accurate Mass: Found 1226.0957 $[M]^+$, Calcd. for $C_{56}H_{53}O_4{}^{11}B^{98}MoN_6P_2{}^{80}Se^{102}Ru$ 1226.0959. Anal. Found: C, 55.28; H, 4.70; N, 6.23%. Calcd. for $C_{56}H_{53}BMoN_6O_4P_2RuSe$: C, 55.01; H, 4.37; N, 6.87%. *Crystal data for* **8**: $C_{56}H_{53}BN_6MoO_4RuP_2Se$: M_r = 1222.80, monoclinic, $P2_1/c$, *a* = 15.5960(2), *b* = 17.0224(3) , *c* =23.1922(3) Å, β = 101.019(1)°, *V* = 6043.58(15) Å^3, *Z* = 4, $D_{calcd.}$ = 1.344 Mg m^{-3}, μ(Mo Kα) = 1.16 mm^{-1}, *T* = 200(2) K, yellow plate, 0.23 x 0.07 x 0.03 mm, 13,858 independent reflections. F^2 refinement, R_1 = 0.036, wR_2 = 0.208 for 5,758 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 50°), 652 parameters, CCDC 758126.

Acknowledgements

This work was supported by the Australian Research Council (DP110101611 and DP170102695). The authors declare no conflict of interest.

Notes and references

1 For reviews on CS, CSe and CTe ligands see: (a) W. Petz, *Coord. Chem. Rev.,* 2008, **252**, 1689 – 1733. (b) P. V. Broadhurst, *Polyhedron*, 1985, **4**, 1801 – 1846. (c) I. S. Butler, *Pure Appl. Chem.*, 1988, **60**, 1241 – 1244. (d) I. S. Butler, *Acc. Chem. Res.*, 1977, **10**, 359 – 365. (e) E. K. Moltzen, K. J. Klabunde and A. Senning, *Chem. Rev.*, 1988, **88**, 391 – 406.

2 (a) I. S. Butler, D. Cozak, S. R. Stobart and K. R. Plowman, *Inorg. Synth.*, 1979, **19**, 193 – 197. (b) I. S. Butler, D. Cozak and S. R. Stobart, *Inorg. Chem.*, 1977, **16**, 1779 – 1782. (c) I. S. Butler, D. Cozak and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 1975, 103 – 104. (d) I. S. Butler, A. M. English and K. R. Plowman, *Inorg. Synth.,* 1982, **21**, 1 – 6. (e) O. Kolb and H. Werner, *J. Organomet. Chem.*, 1984, **268**, 49 – 62. (f) H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 927 – 949. (g) M. Ebner and H. Werner, *Chem. Ber.*, 1988, **121**, 1449 – 1450. (h) A. A. Ismail, I. S. Butler, J.-J. Bonnet and S. Askenazy, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 1582 – 1585. (g) J.-Y. Saillard and D. Grandjean, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.,* 1978, **34**, 3772 – 3775.

3 (a) G. R. Clark, K. R. Grundy, R. O. Harris, S. M. James and W. R. Roper, *J. Organomet. Chem.* 1975, **90**, C37– C39. (b) P. J. Brothers, C. E. L. Headford and W. R. Roper, *J. Organomet. Chem.,* 1980, **195**, C29 – C33. (c) W. R. Roper and K. G. Town, *J. Organomet. Chem.*, 1983, **252**, C97 – C100. (d) G. R. Clark and S. M. James, *J. Organomet. Chem.*, 1977, **134**, 229 – 236.

4 (a) G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.*, 1980, **102**, 1206 – 1207. (b) G. R. Clark, K. M. Marsden, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1988, **338**, 393 – 410. (c) J. P. Battioni, D. Mansuy and J. C. Chottard, *Inorg. Chem.*, 1980, **19**, 791 – 792.

5 (a) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 457– 458. (b) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75 – 76.

6 (a) J. B. Greco, J. C. Peters, T. A. Baker, W. M. Davs, C. C. Cummins and G. Wu, *J. Am. Chem. Soc.*, 2001, **123**, 5003 – 5013. (b) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177 – 5179. (c) Y. Mutoh, N. Kozono, T. Araki, N. Tsuchida, K. Takano and Y. Ishii, *Organometallics*, 2010, **29**, 519 – 522.

7 (a) C. M. A. McQueen and A. F. Hill, *Organometallics*, 2012, **31**, 2482 – 2485. (b) S. Takemoto, J. Ohata, K. Umetani, M. Yamaguchi and H. Matsuzaka, *J. Am. Chem. Soc.,* 2014, **136**, 15889 – 15892.

8 (a) B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 2397 – 2402. (b) S. Lotz, R. R. Pille and P. H. Van Rooyen, *Inorg. Chem.*, 1986, **25**, 3053 – 3057. (c) R. A. Doyle and R. J. Angelici, *Organometallics*, 1989, **8**, 2207 – 2214. (d) R. J. Angelici and J. W. Dunker, *Inorg. Chem.*, 1985, **24**, 2209 – 2215. (e) M. G. Choi, L. M. Daniels and R. J. Angelici, *J. Organomet. Chem.*, 1990, **383**, 321 – 337. (f) H. P. Kim, S. Kim, R. A. Jacobson and R. J. Angelici, *J. Am. Chem. Soc.*, 1986, **108**, 5154 – 5158. (g) R. A. Doyle, L. M. Daniels, R. J. Angelici and F. G. A Stone, *J. Am. Chem. Soc.*, 1989, **111**, 4995 – 4997. (h) V. G. Albano, S. Bordoni, L. Busetto, A. Palazzi, P. Sabatino and V. Zanotti, *J. Organomet. Chem.*, 2002, **659**, 15 – 21. (i) G. Hogarth, M. H. Lavender and K. Shukri, *J. Organomet. Chem.*, 2000, **595**, 134 – 139. (j) V. G. Albano, S. Bordoni, L. Busetto, C. Camiletti, M. Monari, F. Prestopino and V. Zanotti, *J. Chem. Soc., Dalton Trans.*, 1996, 3693 – 3698. (k) L. Busetto, S. Bordoni, V. Zanotti and M. C. Cassani, *J. Organomet. Chem.*, 1993, **451**, 107 – 110. (l) S. Bordoni, L. Busetto, M. C. Cassani, V. Zanotti, V. G. Albano, M. Monari, F. Prestopino and P. Sabatino, *Gazz. Chim. Ital.*, 1995, **125**, 57. (m) V. G. Albano, S. Bordoni, L. Busetto, C. Camiletti, M. Monari, A. Palazzi, F. Prestopino and V. Zanotti, *J. Chem. Soc., Dalton Trans.,* 1997, 4665 – 4670. (n) V. G. Albano, M. Monari, L. Busetto, L. Carlucci and V. Zanotti, *Gazz. Chim. Ital.*, 1992, **122**, 201. (o) H. Werner, O. Kolb, and P. Thometzek, *J. Organomet. Chem.*, 1988, **347**, 137 – 150. (p) A. R. Johnson, W. M. Davies, C. C. Cummins, S. Serron, S. P. Nolan, D. G. Musaev and K. Morokuma, *J. Am. Chem. Soc.*, 1998, **120**, 2071 – 2085. (q) A. R. Manning, L. O'Dwyer, P. A. McArdle and D. Cunningham, *J. Chem. Soc., Chem. Commun.*, 1992, 897 – 898. (r) A. R. Manning, L. O'Dwyer, P. A. McArdle and D. Cunningham, *J. Organomet. Chem.*, 1998, **551**, 139 – 149. (s) T. E. North, J. B. Thoden, B. Spencer, A. Bjarnason and L. F. Dahl, *Organometallics*, 1992, **11** 4326 – 4337. (t) O. Kolb and H. Werner, *Angew. Chem., Int. Ed. Engl.,* 1982, **21**, 202 – 203.

9 (a) L. M. Caldwell, A. F. Hill, J. Wagler and A. C. Willis, *Dalton Trans.*, 2008, 3538 – 3541. (b) L. M. Caldwell, A. F. Hill, A. D. Rae and A. C. Willis, *Organometallics*, 2008, **27**, 341 – 345. (c) L. M. Caldwell, R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2010, **29**, 1526 – 1529.

10 I. A. Cade, A. F. Hill and C. M. A. McQueen, *Organometallics*, 2009, **28**, 6639 – 6641.

11 R. D. Bedford, P. J. Dyson, A. F. Hill, A. G. Hulkes and C. J. Yates, *Organometallics*, 1998, **17**, 4117 – 4120.

12 A. G. Maki and R. L. Sams, *J. Mol. Spectrosc.*, 1981, **90**, 215 – 221.

13 C. Hirose and R. F. Curl, *J. Chem. Phys.*, 1971, **55**, 5120 – 5123.

14 T. Wentink, *J. Chem. Phys.*, 1959, **30**, 105 – 115.

15 J. S. Rutherford and C. Z. Calvo, *Z. Kristallogr.*, 1969, **128**, 229.

16 D. Christen, H. Oberhammer, W. Zeil, A. Haas and A. Darmadi, *J. Mol. Struct.*, 1980, **66**, 203 – 210.

17 J. McGurk, N. C. Figelaar, S. L. Rock, C. L. Norris and W. N. Flygare, *J. Chem. Phys.*, 1973, **58**, 1420 – 1424.

18 For reviews of organometallic chemistry of supported by the Tp* ligand see: (a) Caldwell, L. M. *Adv. Organomet. Chem.*, 2008, **56**, 1 – 94. (b) M. Lail, K. A. Pittard and T. B. Gunnoe, *Adv. Organomet. Chem.*, 2008, **56**, 95 – 153. (c) E. Becker, S. Pavlik and K. Kirchner, *Adv. Organomet. Chem.*, 2008, **56**, 155 – 197. (d) I. R. Crossley, *Adv. Organomet. Chem.*, 2008, **56**, 199 – 321. (e) S. Trofimenko, *Scorpionates: The Coordination of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999. (f) C. Pettinari, *Scorpionates II. Chelating Borate Ligands*, Imperial College Press, London, 2008.

19 (a) T. A. O'Brien and J. F. O'Brien, *J. Coord. Chem.*, 1998, **44**, 91 – 99. (b) J. Leszczynski, B. Hale and D. Leszczynska, *Int. J. Quantum Chem., Quantum Chem. Symp.*, 1991, **25**, 451. (c) M. Springborg, *Phys. Rev. B: Cond. Matter Mat. Phys.*, 1989, **39**, 5327 – 5344. (d) J. Jokisaari, P. Lazzeretti and P. Pyykko, *Chem. Phys.*, 1988, **123**, 339 – 350. (e) J. Kalcher, *Phys. Chem. Chem. Phys.*, 2002, **4**, 3311 – 3317. (f) J. C. Green, A. L. Hector, A. F. Hill, S. Lin and J. D. E. T. Wilton-Ely, *Organometallics*, 2008, **27**, 5548 – 5558. (g) J. Y. Saillard, D. Grandjean, P. Caillet and A. Le Beuze, *J. Organomet. Chem.*, 1980, **190**, 371 – 379. (h) A. L. Colebatch, A. F. Hill and M. Sharma, *Organometallics*, 2015, **34**, 2165 – 2182

20 J. A. Pople, *J. Mol. Phys.*, 1964, **7**, 301.

21 (a) D. Cozak, I. S. Butler and I. M. Baibich, *J. Organomet. Chem.*, 1979, **169**, 381 – 393. (b) D. Cozak and I. S. Butler, *Spectr. Letts*, 1976, **9**, 673 – 679.

22 (a) W. W. Greaves and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 2983 – 2988. (b) H. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.,* 1987, **27**, 51 – 111

23 B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun*., 2018, **54**, 1702 – 1705.

24 K. C. Stone, P. S. White and J. L. Templeton, *J. Organomet. Chem.*, 2003, **684**, 13 – 19.

25 (a) G. Tresoldi, F. Faraone and P. Piraino, *J. Chem. Soc., Daltron Trans.*, 1979, 1053 – 1056. (b) F. Faraone, G. Tresoldi and G. A. Loprete, *J. Chem. Soc., Dalton Trans.*, 1979, 933 – 937.

26 (a) J. Fortune and A. R. Manning, *Organometallics*, 1983, **2**, 1719 – 1723. (b) A. F. Hill and J. D. E. T. Wilton-Ely, *Organometallics*, 1996, **15**, 3791 – 3797. (c) A. F. Hill, D. A. Tocher, A. J. P. White, D. J. Williams and J. D. E. T. Wilton-Ely, *Organometallics*, 2005, **24**, 5342 – 5355.

27 (a) M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121 – 198. (b) W. R. Roper, *J. Organomet. Chem.*, 1986, **300**, 167 – 190.

28 (a) Y. Lee and J. C. Peters, *J. Am. Chem. Soc.*, 2011, **133**, 4438 –4446. (b) D. L. M. Suess and J. C. Peters, *J. Am. Chem. Soc.*, 2013, **135**, 12580 – 12583. (c) M. M. Deegan and J. C. Peters, *J. Am. Chem. Soc.*, 2017, **139**, 2561 – 2564.

29 (a) R. N. Vrtis, C. P. Rao, S. Warner and S. J. Lippard, *J. Am. Chem. Soc.,* 1988, **110**, 2669 – 2670. (b) R. N. Vrtis, S. Liu, C. P. Rao, S. G. Bott and S. J. Lippard, *Organometallics*, 1991, **10**, 275 – 285 (c) J. D. Protasiewicz and S. J. Lippard, *J. Am. Chem. Soc.*, 1991, **113**, 6564 – 6570. (d) J. D. Protasiewicz, A. Masschelein and S. J. Lippard, *J. Am. Chem. Soc.*, 1993, **115**, 808 – 810. (e) J. D. Protasiewicz, B. S. Bronk, A. Masschelein and S. J. Lippard, *Organometallics*, 1994, **13**, 1300 – 1311.

30 (a) Conquest® February 2018 release; Cambridge Crystallographic Data Centre. (b) F. J. Lalor, T. Desmond, G. M. Cotter, C. A. Shanahan, G. Ferguson, M. Parvez and B. J. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1995, 1709 – 1726. (c) C. A. Rusik, M. A. Collins, A. S. Gamble, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1989, **111**, 2550 – 2560. (d) C. A. Rusik, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1986, **108**, 4652 – 4653.

31 A. J. L. Pombeiro, *NATO ASI Series, Series C: Math. Phys. Sci.,* 1993, **392**, 105 – 121

32 (a) Y. Y. Liu, A. Mar, S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1988, **66**, 1997– 2006. (b) E. C. Onyiriuka, S. J. Rettig and A. Storr, *Can. J. Chem.*, 1986, **64**, 321– 327. (c) M. R. St.-J. Foreman, A. F. Hill, M. K. Smith and N. Tshabang, *Organometallics*, 2005, **24**, 5224 – 5226. (d) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova and M. Y. Zakharova, *Doklady Akad. Nauk. SSSR,* 1964, **156**, 612. (e) R. B. King, A. Efraty and W. M. Douglas, *J. Organomet. Chem.* 1973, **60**, 125 – 137.

33 M. I. Bruce, C. Haneister, A. C. Swincer and R. C. Wallis, *Inorg. Synth.*, **1990**, *28*, 270 – 272.

34 For a review of the organometallic chemistry of the '$Ru(PPh_3)_2(\eta\text{-}C_5H_5)$' fragment see S. G. Davies, J. P. McNally and A. J. Smallridge, *Adv. Organomet. Chem.*, 1990, **30**, 1– 76.

35 Y. Sunada, Y. Hayashi, H. Kawaguchi and K. Tatsumi, *Inorg. Chem.*, 2001, **40**, 7072 – 7078.

36 A. F. Hill, R. A. Manzano, M. Sharma and J. S. Ward, *Organometallics*, 2015, **34**, 361– 365.

37 (a) L. M. Caldwell, A. F. Hill, A. G. Hulkes, C. M. A. McQueen, A. J. P. White and D. J. Williams, *Organometallics*, 2010, **29**, 6350 – 6358. (b) I. Baxter, A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1997, 2049 – 2050. (c) M. A. Beswick, P. R. Raithby, A. Steiner, J. C. Vallat, K. L. Verhorevoot and D. S. Wright, *J. Chem. Soc., Dalton Trans.*, 1996, 2183 – 2184. (d) M. A. Beswick, C. N. Harmer, P. R. Raithby, A. Steiner, M. Tombul and D. S. Wright, *J. Organomet. Chem.*, 1999, **573**, 267 – 271. (e) H. Sugiyama, Y. Hayashi, H. Kawaguchi and K. Tatsumi, *Inorg. Chem.*, 1998, **37**, 6773 – 6779. (f) S. Schäfer, C. Moser, J. J. Tirree, M. Nieger and R. Pietschnig, *Inorg. Chem.*, 2005, **44**, 2798 – 2802. (g) R. Pietschnig, K. Merz and S. Schäfer, *Heteroat. Chem.*, 2005, **16**, 169– 174.

38 E. O. Fischer and E. Moser, *Inorg. Synth.*, 1970, **12**, 35 – 43.

39 (a) E. D. Schermer and W. H. Baddley, *J. Organomet. Chem.*, 1971, **27**, 83 – 88. (b) K. Geetharani, S. K. Bose, D. Basak, V. M. Suresh and S. Ghosh, *Inorg. Chim. Acta*, 2011, **372**, 42 – 46.

40 (a) T. J. Collins and W. R. Roper, *J. Organomet. Chem.*, 1978, **159**, 73 – 89. (b) W. R. Roper and K. G. Town, *J. Chem. Soc., Chem. Commun.*, 1977, 781 – 782. (c) T. J. Collins and W. R. Roper, *J. Organomet. Chem.*, 1977, **139**, C9 – C12. (d) T. J. Collins and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1976, 1044 – 1045.

41 (a) G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.*, 1980, **102**, 6570 – 6571. (b) D. D. Ellis, J. M. Farmer, J. M. Malget, D. Mullica, D. F. and F. G. A. Stone, *Organometallics*, 1998, **17**, 5540 – 5548. (c) A. F. Hill, B. A. Nasir and F. G. A. Stone, *Polyhedron*, 1989, **8**, 179 – 187. (d) L. M. Caldwell, A. F. Hill and A. C. Willis, *Chem. Commun.*, 2005, 2615 – 2617. (e) D. J. Cook, and A. F. Hill, *Organometallics*, 2003, **22**, 3502 – 3512. (f) W. R. Roper and A. H. Wright, *J. Organomet. Chem.,* 1982, **233**, C59 – C63.

42 (a) The corresponding perchlorate salt has been described previously: B. E. Cavit, K. R. Grundy and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1972, 60 – 61. The salt $[RuH(NCMe)(CO)_2(PPh_3)_2]PF_6$ was prepared via a similar route employing $AgPF_6$ in place of $AgClO_4.H_2O$.

43 P. G. Jessop, S. J. Rettig, C. Lee and B. R. James, *Inorg. Chem.* **1991**, *30*, 461 7– 4627.

44 (a) Z. Zhang, Q.-S. Li, Y. Xie and R. B. King, *Polyhedron*, 2012, **31**, 1 – 11. (b) Z. Zhang,Q.-S. Li, Y. Xie, and R. B. King, *J. Organomet. Chem.*, 2011, **696**, 2958 – 2965. (c) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *Eur. J. Inorg. Chem.*, 2010, 4175 – 4186. (d) H. Gong, Q. Luo, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *Inorg. Chem.*, 2015, **54**, 132 – 142. (e) Z. Zhang, L. Pu, Q.-S. Li and R. B. King, *New J. Chem.*, 2014, **38**, 4282 – 4289. (f) Z. Zhang, Q.-S. Li, R. B. King and H. F. Schaefer III, *Eur. J. Inorg. Chem.*, 2012, **36**, 1104 – 1113. (g) Z. Zhang, Q.-S. Li, Y. Xie and R. B. King, *Inorg. Chim. Acta*, 2011, **375**, 193 - 204. (h) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *J. Phys. Chem., A,* 2010, **114**, 2365 – 2375. (i) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *New J. Chem.*, 2010, **34**, 92 – 102. (j) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *J. Phys. Chem., A*, 2010, **114**, 486 – 497. (k) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *Inorg. Chem.*, 2009, **48**, 5973 – 5982. (l) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *Inorg. Chem.,* 2009, **48**, 6167 – 6177. (m) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer III, *Inorg. Chem.*, 2009, **48**, 1974 – 1988.

45 R. D. Young, A. F. Hill, G. E. Cavigliasso and R. Stranger, *Angew. Chem., Int. Ed.,* 2013, **52**, 3699 – 3702

46 D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, 1973, **95**, 197 – 199.

47 P. J. Fagan, W. S. Mahoney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, **9**, 1843 – 1852.

Table of Contents Graphic